R&D+*i* FOR CERAMIC TILES IN THE 21st CENTURY: COMPETITION, DIVERSITY, AND FUNCTIONALITY

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ABSTRACT

The Spanish ceramic tile manufacturing sector (which also refers to raw material suppliers and producers of bodies, glazes, frits, engobes and pigments) is facing a most singular moment in its history. First of all, it needs to overcome the economic downturn that started in 2008 before going on to deal with the fierce competition from other countries emerging as competitive producers in the post-crisis scenario. Nowadays, the sector has a more or less homogenous character in which the different companies tend to produce very similar materials and therefore compete for the same market. This paper proposes two alternative but compatible road maps that provide a possible future strategy to diversify the sector's supply offer by planning its R&D+i to: i) *achieve significant production cost savings* for standard ceramic products, and ii) *to develop new specialised ceramic materials* that meet the specific cultural and practical needs of each particular market environment. In the short term, the ideal strategy would be to develop the first alternative in order to produce ceramic bodies at significantly lower firing temperatures than at present, the immediate effect of which would be to reduce glaze thickness and the amount and size of pigment particles, thereby opening the way to mass usage of thin-film decorating techniques (such as ink jets) and even laser techniques. In the medium and long term, the second alternative needs to be followed, to increase the overall added value of ceramic tiles, which depends on the skills and ingenuity of researchers and technicians alike to come up with a wide-ranging *diversity* of ceramic products.

1. INTRODUCTION

When one analyses the relative significance of the role played by classic ceramic (CC) materials (traditional ceramics: floor and wall tiles, bricks, refractory materials, tableware and ceramic bathroom fittings, etc. that basically attend primary human needs, especially home-building needs) and advanced ceramic (AC) materials (or technical ceramics, which *apparently* mainly refers to materials covering secondary human needs, e.g. in telecommunications), the world of ceramics seems to be "two-headed", "twin-moded" and "asymmetrical". It is twin-headed in the sense that researchers tend to choose to devote their professional skills to either CC or AC. It is "twin-moded" in the sense that its manufacturing companies, and even producer countries, also tend to opt for either CC or AC. Nevertheless, the sector is also highly asymmetrical, in that the number of publications and concerted research devoted to CC is much lower than for AC, although turnover in economic terms is much higher worldwide for CC than for AC. Figure 1 shows turnover by sub-sectors throughout the world according to a report by the Cookson company published in 2006, where AC can be seen to account for only 19%.

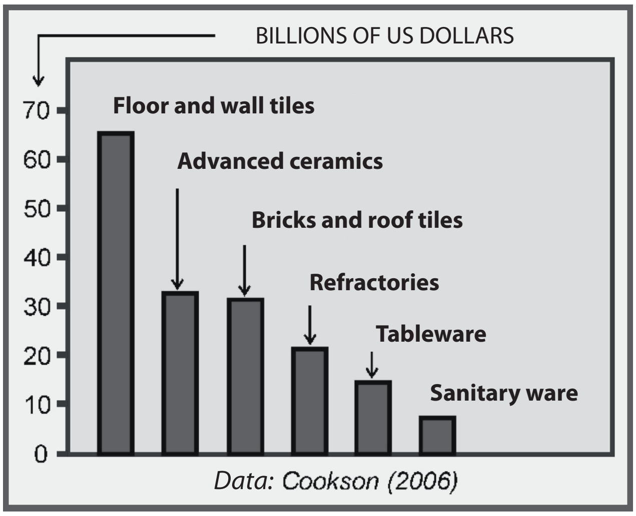

Figure 1. Estimated world turnover in billion dollars for different ceramic materials, according to a report published by Cookson's in 2006.

In Europe, a report by Ecorys, commissioned by the European Community, to study the competitiveness of the European ceramics sector also revealed this same asymmetric character. Turnover in the sector in 2006 reached 28,000 million Euros, split as follows: floor and wall tiles 36 %, bricks and roof tiles 24 %, refractory materials 12 %, technical ceramics 10 %, bathroom fittings 8 %, and ceramic tableware 6 % (N.B. ~74 % is based on triaxial ceramics!!!). That same year, the sector had 221,000 employees, of which ~ 83 % were dedicated to CC. France, Germany, Holland and the UK are the main producers of AC, while Spain and Italy head the list of CC producer countries. This asymmetry arises once again when world AC production figures are studied. The European Union provides only one tenth of total world supply, in which the sum total of Japan and the USA accounts for over 80 % [1]. Analysis of these data, comparing the intellectual efforts made in the ceramic industry with the social rewards reaped, reveals a paradox that defies interpretation.

This paper reflects on how R&D+i is applied to *ceramic tiles* (floor and wall F/W tiles) as well as to their *intermediate products*, i.e. spray-dried bodies, frits, glazes and pigments, and to its *raw materials* (industrial minerals and chemical compounds), where these intermediate products and raw materials are used in tile manufacturing plants like assembly lines. The leadership of the Spanish Ceramic Sector (SCS) in tile production (which forms a socio-economic cluster situated mainly in the Mediterranean coastal region) is based on a large number of factors. However, there are three technical factors which afford it a personality of its own, namely: i) the existence very close to the centres of production of top-quality red clay with which to make ceramic bodies, ii) the development of specific top-quality materials adapted for use with these clays, and iii) the widespread support for the sector that comes from institutions with R&D+i capabilities in a wide range of collaboration projects that vary from the resolution of simple analytical issues to the development of specific materials and large scale projects entailing changes in production technology. This paper looks at the inter-relationships between these three factors in order to: i) review superficially the progress made to date and currently available industrial processes, ii) propose global measures that provide both economic and ecological or material cost savings (sustainable development); and iii) establish possible ways to diversify production through research into new materials and the use of new technologies applicable to the sector (specialisation).

2. CURRENT CERAMICS

Ceramic tile manufacturers are already familiar with the results of the in-depth innovation process that took place in the 1980s, when dry route body processing was replaced with wet route body processing using clay spray-drying technology. As a result of this change, a "ceramic tile revolution" took place, which completely changed the type of tiles manufactured prior to that date (see figure 2). The result was that traditional double-fired products almost disappeared to be replaced by porous single fired tiles, while the use of single-fired flooring (stoneware) also expanded significantly. Nowadays, red body tile output accounts for between 70 and 80% of the total, the rest being white body production (in which imported raw materials are used in most cases - between 60 and 85% of the total formulation), while the production of porcelain stoneware is a minority (around 8.5%?). In other words, the current situation is still the result of the inheritance of the aforementioned change in technology, based mainly on the use of local raw materials. It should be mentioned that remarkable efforts have been made to use national raw materials in white body formulations for stoneware and porcelain tile [2-6], where their incorporation into white bodies has been enhanced by purifying local clay using magnetic separation.

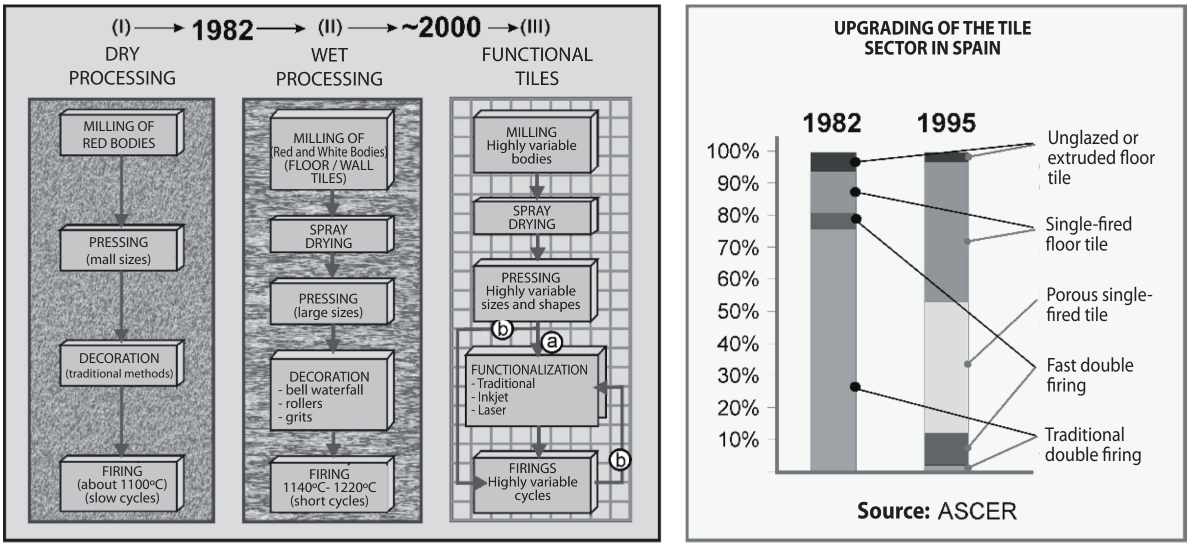

Figure 2. Diagram of the technology change from dry route to wet route production in 1982 and the resulting upgrading of the type of ceramic tile production in Spain.

However, the current trend shows that the stoneware/porcelain tile or white body/red body tandems are tending to disappear as synonyms of differing quality, and numerous bodies have arisen with 'hybrid' formulations (including classic compositions, i.e. mixtures of red clays for stoneware and white clay-kaolin with feldspars for porcelain, in some cases by adding low proportions of carbonates) which have led to greyish and reddish hues with open porosity rates of less than 0.5 % and mechanical properties comparable to white porcelain levels. However, traditional red body compositions (mixtures of flux and plastic clays with other compacting and refractory materials which, when fired at 1140ºC, provide an open porosity of 3-4% and ~ 7% of linear shrinkage) is still the dominant material and therefore the one on which future research efforts should be based. White-body formulations in Spain will always depend on supplies of imported clay (this refers to clays with high fired whiteness, plasticity and fusibility), as geological deposits of this material no longer exist locally. Similarly, deposits of sodium feldspars have also been exhausted. These difficulties have been partially offset by using other materials such as wollastonite [7] and frit fluxes, pages 237 to 244 in ref. [3].

Apart from the ceramic glazes developed for rapid single-firing (see review in ref. [8]), numerous glass-ceramic glazes (or rather fritted materials that are added to mixtures of frits and industrial minerals to create fired glazes, or in grits, etc) have been developed to provide opacity through crystallisations of zircon $ZrSiO_4$ [9], corundum Al_2O_3 [10], spinel $MgAl_2O_4$ [11], diopside $CaMgSi_2O_6$ [*], mullite $Al_6Si_3O_{18}$ [10], wollastonite $CaSiO_3$, celsian $BaAl_2Si_2O_8$, anorthite $CaAl_2Si_2O_8$ [9], among others, and transparency through crystallisations of β-cristobalite $Si_{1-x}Al_x(Ca,Sr)_{x/2}O_2$ [13], while simultaneously improving mechanical strength properties. Glazes with specific properties also exist, such as those used in areas with high concentrations of static electricity, where glazes containing SnO_2 and Sb_2O_3[14] or with photocatalytic (bactericide) properties based on TiO_2 or other active materials [15] are used.

Likewise, ceramic decoration is also undergoing a significant transition from traditional (albeit modified) screen printing techniques using pigments with particle sizes of around 5 µm to other techniques based on ink technologies and printers with different kinds of heads, for which the ideal particle size is under 1 µm. This requires improved grinding of the material on its exit from the kiln (once specific grinding processes have been researched) and more stable (or less soluble) pigments at firing temperatures, a target which entails the greatest difficulty, especially to decorate porcelain tiles (Tc ~ 1170 ºC). Alternative manufacturing procedures have also been researched for pigments that would produce the required grain size directly; such as the 'sol-gel' technique [16], and for inks containing dissolved chromophores. Another directly related case is that of metallic glazes with significantly different decorating capabilities.

3. COMPETITIVE CERAMICS

Since 1982, the sector has carried out widespread investment in plant & machinery, materials and human resources, in the same way as its counterparts in competing European countries or in other parts of the world since the 1990s. These new producer countries have benefited from inherent advantages (whether in the use of local raw materials, labour costs or variable restrictions in environmental matters), although they use identical production technologies, mainly of European origin. Therefore a change is required which will allow currently available technologies and materials to be used to produce ceramic tiles at a *significantly lower* overall cost than at present, regardless of the increase or reduction in the cost of intermediate products (see diagram in figure 3). The authors consider that such a change should commence with *new ceramic bodies* for firing at lower maximum temperatures (T_c^{max}), while still guaranteeing improved mechanical properties and current open porosity values (as obtained with water absorption trials). The technical existence of such a material would afford numerous advantages, apart from energy cost savings and reduced CO_2 emissions, such as thickness reductions that would require fewer raw materials and enhance oxidisation of the organic matter to prevent 'black core' issues.

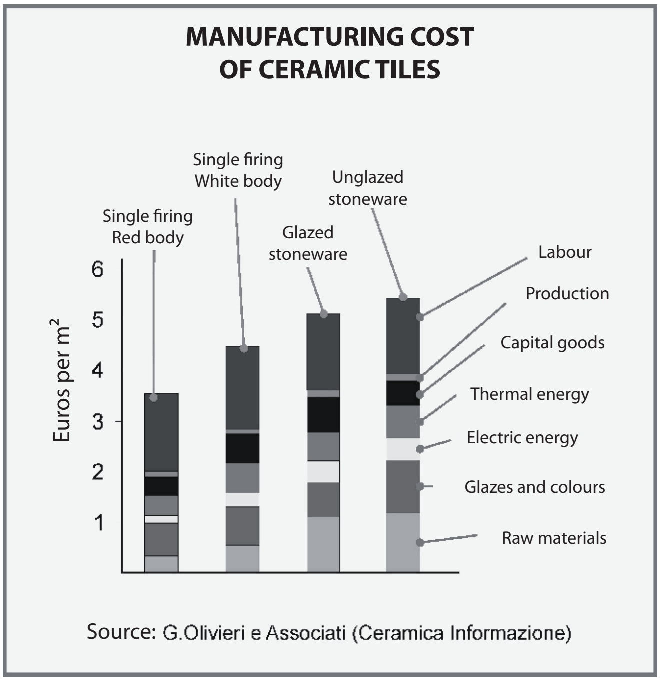

Figure 3. Diagram of approximate cost split for different types of ceramic tile, where, apart from employment, the greatest costs relate to raw materials, glazes and colours, which indicates where cost saving strategies should be focused.

In the case of red bodies, lower firing temperatures would enable reduced opacifying glaze thickness, thereby reducing the use of costly raw materials, whose market price fluctuates greatly (zircon). Likewise, this change would enable the use of smaller amounts of pigment (so competition would be centred on design) or pigments with smaller particle sizes (such as those required for ink-jet techniques) or less stable pigments that are more reactive with the flux materials at maximum firing temperature to increase the colour range in the end product. Obviously, such a change calls for the development of new, low-temperature glazes that need to adapt to the new bodies' linear shrinkage and heat expansion/shrinkage values. In this respect, it should be remembered that tiles are used to cover surfaces and that any reduction in maximum firing temperature associated with reduced linear shrinkage would be most welcome, as that would enable production of an even wider range of sizes. Very similar benefits could be obtained when using white bodies. It is important to highlight the fact if the thickness of the covering layer can be reduced, more advanced (and relatively more costly) materials can be employed, which would then extend the number of decorating techniques available for use, such as thin-film printing or laser-induced crystallisation techniques [17] and other such technologies [18-20] – see diagram summary in figure 4.

Consequently, as maximum firing temperature (T_c^{max}) comes down, the overall competitive and cost-saving benefits would increase in the same direction, like a positive feedback process. Nevertheless, from the technical point of view, reducing Tcmax in red bodies is not the same as reducing it in white bodies, as sintering in red bodies is mainly linked to surface phenomena affecting compacted particles, while in the latter case, sintering is a liquid stage that occurs when feldspars and other fluxes melt. Therefore, re-formulation in one case may be very different from the other. On the other hand, T_c^{max} in wall tiles could be reduced by using carbonates with lower decomposition temperatures. Obviously, under no circumstances should increased fusibility be achieved in bodies by sacrificing dimensional stability or firing heat ranges. Thus, low T_c^{max} bodies depend on the development of advanced fluxes and high-density spray powders, for which the role of particle surface stress needs to be studied. In conclusion, to be competitive, ceramic products need to blend savings on materials (many of which are now scarce) with reduced fuel and energy costs, thereby reducing emissions of pollutant gases – all of these being ideas compatible with the concept of "sustainable development".

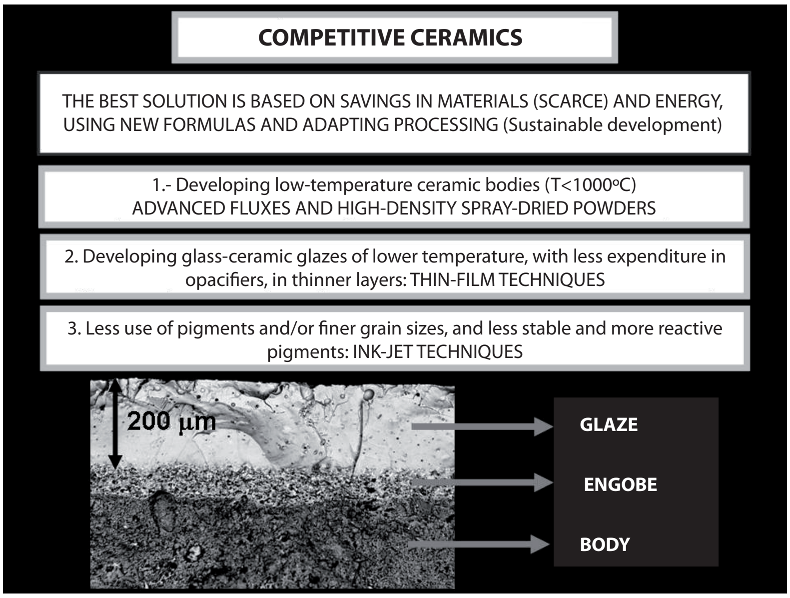

Figure 4. General diagram for competitive ceramic products.

4. SMART CERAMICS

Recent history shows that any planning carried out in the industrial world needs to take certain issues into account, such as energy (linked to raw materials from well-defined geographical locations) and super-population (therefore, 'mega-markets' especially in Asia), and consequently to consider them from the viewpoint of sustainable development. Companies manufacturing CC cannot suddenly switch to producing advanced ceramics and compete in a market that is alien to them and has very different characteristics [21]. They can, however, echo the social demands that such materials cover in order to gradually incorporate them into their products. In short, it is a question of transferring technological innovation to the 'smart home' – see diagram in figure 6 – where a house can be valued in terms of new capabilities and surfaces are not simply decorative items but rather active elements with specific functions. Furthermore, special attention can be given to the economic growth in different geographical, climatic and cultural areas of the planet, where inhabitants' needs and priorities are, in many cases, identical to those of Western society and who are emerging as potential consumer markets if their expectations are met. The origin of this new trend in tile functionality arose more or less at the turn of the century (see diagram in figure 2). With this premise, three fields can be distinguished as the areas where smart and multi-purpose ceramics can gain ground if the two ends of positive feedback between demand and practicality are made to meet [21-23]. This paper distinguishes three groups: a) ceramics for healthcare; b) ceramics for energy; and c) ceramics for comfort. In such a context, outdoor products (for façades and roofs) should cease to be regarded as separate items from indoor articles.

4.1. Ceramics for healthcare.

This group includes innovations relating to health & safety, personal hygiene and quality of air. With regard to the first matter, a historical look at the automobile industry shows that investment in health and safety has always had a social and market component which guarantees success. There exist numerous environments in which health and safety can be instilled into ceramic tiling, for example, in centres using ionising radiation such as hospitals, radiotherapy centres and research institutes. In these cases, radiation-proof wall plating could be supplied using ceramics with high density crystalline phases with heavy, radiation-passivating chemicals.

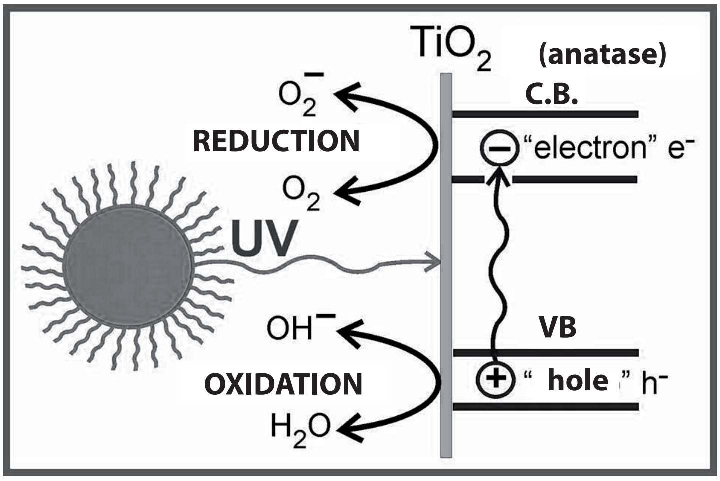

Figure 5. Simplified diagram of photocatalytic effect on TiO_2 (anatase) surfaces. When ultraviolet radiation strikes the Ti-O binding electrons, electronic transitions take place from the valence band (VB) to the conduction band (CB), thereby enabling oxidisation and reduction reactions with the decomposition of certain organic molecules in the atmosphere, NO_x, etc.

The questions of personal hygiene and air quality relate to the photocatalytic effect [24] of bactericide and air cleaning products. The first question stems from biocide materials that initially used Ag particles and later Ag+TiO_2 particles and is already being explored by several companies. The second question is receiving growing attention, as in many cases the use of air conditioning systems is considered to be an unhealthy solution. Figure 5 illustrates a diagram of the photocatalytic effect on TiO_2 with an anatase structure. Given that this material is activated by ultraviolet (UV) radiation, alternatives are being sought for its use indoors where the effect is achieved by radiation within the visible energy range. Additionally, modifying surfaces using laser technology to increase the active surface area would be a highly positive step towards generating nano-roughness [25] and therefore a greater active surface, which is a technique of special interest when the thickness to be modified is sufficiently small.

4.2. Ceramics for energy.

It is important to highlight that in Europe, it is estimated that housing overall uses ~40 % of all consumed energy, which in turn accounts for ~25 % of CO_2 emissions. Therefore, questions relating to *energy production* and *energy saving* in domestic homes should be treated separately. From the point of view of production, the ceramic world is leading a change in attitude. The sun is no longer an item of concern whose energy bleaches and damages the ceramic beauty of outside façades and has become an ally to home maintenance, i.e. a means of producing energy, whether photovoltaic, thermal or both. Theoretically, the solution is ideal for a material whose function is to cover large surface areas, as it represents unlimited, clean energy, free of transport costs, with no geopolitical dependence and of special interest in geographical regions with many hours of sunlight per year (for example, in areas such as ours).

Early generation photovoltaic energy is mainly based on the production of monocrystal or polycrystalline silicon chips in cells to form panels which, in turn, are fitted as totally foreign appendixes on buildings. In this case, no ceramic or glass substrate is required for these devices to work. However, *second generation* photovoltaic energy calls for savings in raw materials (semiconductors), which at present means sacrificing energy efficiency, and uses thin layers of different semiconductors in tandem (for selective absorption of different wavelengths) on glass, ceramic or even plastic substrates, giving rise to a technology now known as BiPV (built-in photovoltaics) [26], i.e. these devices form an integral part of the building. In this generation, the substrate and the thin multilayer device are not two independent entities but rather building efficiency depends on the degree to which technically they can be coupled together, so their glass and/or ceramic character is essential. Although at present glass substrate panels have been much more widely implemented than ceramic-based panels, the latter possibly afford greater installation opportunities. Consequently, certain confidentiality exists regarding the nature of these ceramic bases when results are presented by specialist companies from the sector [27-28], although data is available about devices with mullite [29] and zircon [30] substrates, among others. Finally, it should be mentioned that a *third generation* is currently being developed, although still at the research level, in which ceramic and glass materials may become an integral part of all the components in these devices [31].

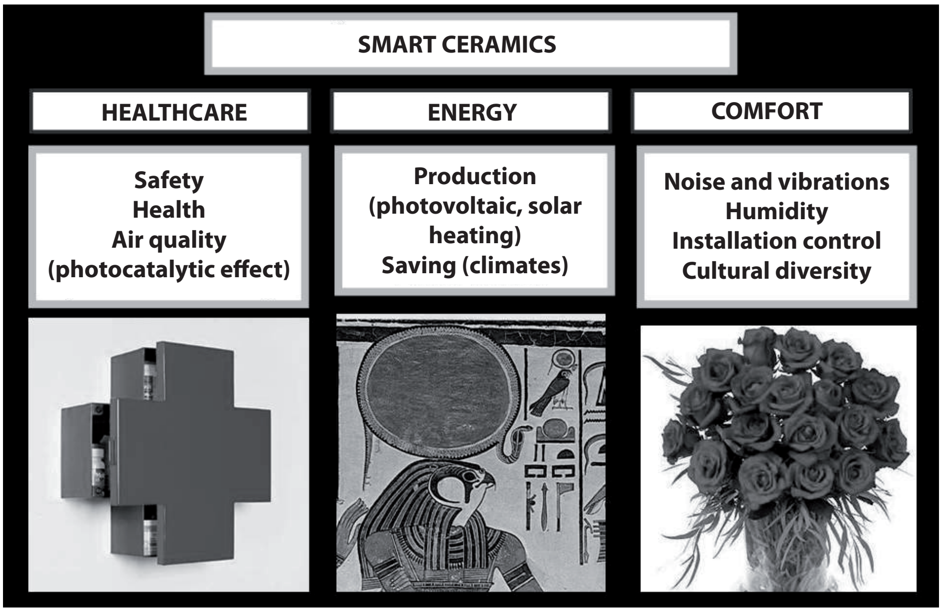

Figure 6. Diagram of the types of smart ceramics, separated into three types of function: healthcare, energy and comfort.

With regard to ceramics for energy-saving, an analysis of heat gains and losses in buildings (efficiency) needs to be made from a climatic point of view, given that this affects potential markets with very different requirements. Therefore, a first distinction should be made between two contrasting situations: "daylight architecture" for cold climates and "sunlight architecture" for warm climates. In the former case, emphasis is on the use of ceramic materials to absorb solar heat energy (during the day), which is then slowly released during the night, while in the latter case, these materials should not accumulate heat but rather enable night-time ventilation of the building. In this sense, studies have been carried out on the near infrared reflectance of different inorganic pigments [32] to obtain ceramics that help to prevent indoor temperatures from rising, thereby providing energy savings by reducing the time that air conditioning units need to be used.

4.3. Ceramics for comfort.

Given that in many industrialised countries, we spend a large part of our time indoors (up to 90% in the so-called first world), it is easy to understand the importance of comfort, which in many cases is associated with productivity. This concept should be interpreted in terms of:

i) *Noise and vibration*: the importance and need for insulation and especially noise insulation and buffering is not limited to large-scale sports installations and swimming pools. These questions are of great importance in many instances in buildings that have already been erected, especially for economic solutions that do not entail large losses of space.

ii) *Humidity*: humidity control by means of ceramic wall coverings is an innovative idea which is already being exploited by manufacturing companies and consists of materials made of special bodies which absorb or emit water depending on the ambient moisture level.

iii) *Installation control*: this is a field that has already been initiated by certain Spanish ceramic companies [33] and is based on the concept of *"home automation"*, which consists of integrating information technologies and telecommunications in the home. In this regard, automatic control systems have been developed for all the installations in a house, including tiles (by means of sensors and WiFi devices) which have the following advantages: greater strength than current (plastic) devices, easier to clean, possibility of incorporating Braille codes, and versatility.

iv) *Cultural diversity: partially or totally subjective factors, preferred designs and/or particular beliefs*. One particular aspect such as colour does not have the same meaning or influence in the East as in the Western world. Although in Western Europe, it is possible that a sufficient number of houses already exist to cover the needs of the next generation, there are numerous emerging markets where individual wooden buildings are going to be replaced and/or extended by constructions where ceramics and glass will play a more prominent role. It should be noted in this respect that comfort is linked to daily issues - the natural stage for ceramics - which fortunately do not have the same relevance nor refer to the same daily routines in all cultures.

5. CONCLUSIONS

Nowadays, the Spanish ceramic tile manufacturing sector is highly homogenous with regard to the products it markets, the prominent features of which are surface decoration (glazes and pigments) and the colour of the firing body (the substrate), when tiles with identical mechanical properties are compared. From a technical point of view, this is the result of the transition from dry route to wet route technology during the 1980s, as well as of the abundance of quality raw materials (clays) in the area surrounding these production centres, and of the R&D+i efforts made by its numerous ceramic technicians. With the turn of the century, competition from emerging countries has become evident and the onset of the present economic crisis may be an indication that the current industrial model in countries such as Spain is becoming obsolete. In view of such a situation, this paper proposes one possible route to be followed in the short term (competitive ceramics) and another which can be taken in the medium and long-term (smart ceramics).

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REFERENCES

[1] FWC Sector Competitiveness Studies – Competitiveness of the Ceramics Sector. Within the Framework Contracto f Pectoral Competititveness Studies – ENTR/06/054. Final report, 13 October 2008. ECORYS.

[2] Sánchez-Muñoz L, Nebot-Díaz I, Carda JB, Tuduri F, Gracia A, Cerisuelo E (2001) Obtención de soportes cerámicos de baja porosidad a partir de materias primas nacionales. Ceram. Inf. 272: 48-54.

[3] Sánchez-Muñoz L, Carda Castelló JB. Materias primas y aditivos cerámicos. Enciclopedia Cerámica. Tomo 2.1. cap. I a VII (2002) y Tomo 2.2. cap VIII a XVI (2003). Ed: Faenza Editrice Ibérica S.L. Castellón.

[4] Sánchez-Muñoz L, Cava S, Paskocimas CA, Cerisuelo E, Longo E, Carda Castelló JB (2002). Influência da composiçao das matérias-primas no processo de gresificaçao de revestimentos cerâmicos. Cerâmica (Revista de la Asociación Brasileña de Cerámica) 48:137-145.

[5] Sánchez-Muñoz L, Cava S, Paskocimas CA, Cerisuelo E, Longo E, Carda Castelló JB (2002) Modelamento do processo de gresificaçao de massa cerâmicas de revestimento. Cerâmica (Revista de la Asociación Brasileña de Cerámica) 48: 217-222.

[6] Sánchez-Muñoz L, Cava S, Paskocimas CA, Cerisuelo E, Longo E, Carda Castelló JB (2002) Seleçao de matérias-primas no desenvolvimento de formulaçoes de massas cerâmicas. Cerâmica (Revista de la Asociación Brasileña de Cerámica) 48: 108-113.

[7] Sánchez-Muñoz L, Cerisuelo E, Tuduri F, Plaza S, Carda JB (2002) Elaboration of porcelain stoneware tiles at 1170 ºC by addition of wollastonite. Key Engineer. Mater. 206-213: 2205-2208.

[8] Escribano López P, Carda Castelló JB, Cordoncillo Cordoncillo E. Esmaltes y Pigmentos Cerámicos. Enciclopedia Cerámica Tomo 1. (2001). Ed. Faenza Editrice Ibérica S.L. Castellón.

[9] Tichell MT, Bakali J, Pascual A, Nebot-Díaz I, Sánchez-Muñoz L, Carda JB (2000) Esmaltes especiales para soportes de gres prcelánico. Bol. Soc. Esp. Ceram. Vidrio 39(1):31-38.

[10] Jovani MA, Carceller JV, Soler A, Nebot A, Núñez I, Sánchez-Muñoz L, Guaita J, Cordoncillo E, Carda JB (2000) Desarrollo de esmaltes híbridos a partir de fritas y geles, adaptados a ciclos de monococción de gres y gres porcelánico. VI World Congress on Ceramic Tile Quality, 199-211.

[11] Tichell MT, Bakali J, Sánchez J, Pórtoles J, Soler C, Nebot-Díaz I, Sánchez-Muñoz L, Carda JB (2000) Esmaltes vitrocerámicos con cristalizaciones de aluminatos y silicoaluminatos, adaptados a soportes de gres porcelánico. VI World Congress On Ceramic Tile Quality, Qualicer, 465-473.

[12] Baldi G, Generali E, Leonelli C, Manfredini T, Pellacani GC, Siligardi C (1995) Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze applications. J.Mater. Sci. 30:3251-3255.

[13] Sánchez-Muñoz L, Cabrera MJ, Foo A, Beltrán H, Carda JB (2002) Esmaltes transparentes para gres porcelánico: Esmaltes vítreos y vitrocerámicos con cristalizaciones de cristobalita. VII World Congress On Ceramic Tile Quality. Qualicer: 239-254.

[14] Gómez JJ, Carda JB, Nebot A, Carceller JV, Jovani MA, Soler A (1999) Conductividad eléctrica en pavimentos cerámicos esmaltados. Desarrollo de un esmalte electroconductivo basado en SnO_2-Sb_2O_3. Ceram Inf. 3:1-24.

[15] Tichell MT, Pascual A, Bakali J (1998) Desarrollo de vidriados cerámicos con propiedades ópticas de absorción y emisión, aplicados como esmaltes para azulejos cerámicos con propiedades bactericidas. V World Congress On Ceramic Tile Quality. Qualicer, Castellón.

[16] Atkinson A, Doorbar J, Hudd A, Segal DL, White PJ (1997) Continuous ink-jet printing using sol-gel "ceramic" inks. J Sol-Gel Sci. Technol. 8: 1093-1097.

[17] Lennikov VV, Pedra JM, Gomez JJ, de la Fuente GF, Carda JB (2007) In situ synthesis of composite $MTiO_3$-Al_2O_3 coatings via laser zone melting. Solid State Sciences 9: 404-409.

[18] Larrea A, de la Fuente GF, Merino RI, Orera VM (2002) ZrO_2-Al_2O_3 eutectic plates produced by laser zone melting. Journal of the European Ceramic Society 22: 191-198.

[19] Bakali J, Fortanet E, de la Fuente X, Lahoz R, Estepa LC, Peris G, Marinova I, Pavlov R, Pedra JM, Carda JB (2004) Structural and Microstructural Characterisation of Refractory Oxides Synthesised by Laser. Key Eng. Mater. 264-268: 317-320.

[21] Ohmura A, Ouchi N, Morisaki S, Watanabe C (2003): Funcionality development as a survival strategy for fine ceramics. Technovation 23: 833-842.

[22] Moreno Berto AV (2006) Ceramic tiles: above and beyond traditional applications. Bol. Soc. Esp. Ceram. Vidr. 45(2):59-64.

[23] Jaquotot P, Campillo A, Reinosa JJ, Romero JJ, Bengochea MA, Esteban-Cubillo A, Santarén J, Aguilar E, Pina R, Pecharromán C, Moya JS, Fernández JF (2009) Desarrollo de esmaltes nanoestructurados multifuncionales. Bol. Soc. Es. Ceram Vidrio 48(2):95-98.

[24] Fujishima A, Honda K (1972): Electrochemical photolysis of water at a semiconductor electrode. Nature 238 (5358) 37-38.

[25] Groenendijk M, Meijer J (2006) Microstructuring using femtosecond pulsed laser ablation. J. Laser Appl. 18(3):227-232.

[26] Bahaj A (2005) Solar photovoltaics energy: generation in the built environment. Civil Engineering 158: 45-51.

[27] Carnel L, Gordon I, Van Gestel D, Van Nieuwenhuysen K, Agostinelli G, Beaucarne G, Poortmans J (2006) Thin-film polycrystalline silicon solar cell on ceramics substrates with a V_{oc} above 500 mV. Thin Solid Films 511-512: 21-25.

[28] Barnett AM, Rand JA, Hall RB, Bisaillon JC, DelleDonne EJ, Feyock BW, Ford DH, Ingram AE, Mauk MG, Yaskoff JP, Sims PE (2001) High current, thin silicon-on-ceramic solar cell. Solar Energy Mater. Solar Cells 66: 45-50.

[29] Focsa A, Gordon I, Beaucarne G, Tuzun O, Slaoui A, Poortmans (2008) Heterojunction a-Si/poly-Si solar cells on mullita substrates. Thin Solid Films 516: 6896-6901.

[30] Kieliba T, Bau S, Schober R, Oβwald D, Reber S, Eyer A, Willeke G (2002) Crystalline silicon thin-film solar cells on $ZrSiO_4$ ceramic substrates. Solar Energy mater. Solar Cells 74: 216-266.

[31] Conibeer G (2007) Third-generation photovoltaics. Nature Mater. 10 (11): 42-50.

[32] Levinson R, Akbari H, Reilly JC (2007) Cooler tile-roofed buildings with near-infrared-reflective non-white coatings. Build. Envir. 42: 2591-2605.

[33] www.tauceramica.net